

Apple or pear purée and its preparation procedure

5 This invention concerns a procedure for improving the texture of apple or pear purée, together with the products obtained using this procedure (thickened, jellified and sugared pulps, etc) and their applications in food industries.

10 The pectins are parietal polysaccharides that are part of the composition of numerous plants in variable proportions depending on their origin. Their main structural feature is the presence of a skeleton of partially methylated galacturonic acids, i.e. in which carboxylic acid functions are partially esterified by methanol.

15 These polysaccharides may be used in their pure state as gelling agents or thickening agents in food preparations. The possibility of and conditions for gel formation depend on the degree of methylation of the pectins, which is itself a function of the plant from which they are extracted and the extraction process. They are generally highly methylated, but this degree of methylation (DM) may change as the fruits ripen.

20 Highly methylated pectins (HM = High Methoxyl), i.e. those in which more than 50% of the carboxylic functions of the galacturonic acids are methylated, may form gels in the presence of sugars (with a concentration of more than 55%), in an acid environment (pH = 2.5 to 3). This process is currently used in the manufacture of jellies, jams, etc.

25 Activation tests on the natural pectinesterase activity of plants have been carried out with a view to improving the firmness of plant pieces (apples (Wiley R.C. and Lee Y.S., 1970), tomatoes (Hsu et al., 1965), carrots (Lee C.Y. et al., 1979)). These tests were conducted in order to show the influence of calcium in maintaining the firmness of fruits. They also showed that endogenous pectinesterases are only truly active at a relatively high pH (pH > 6).

30 Currently, producing fruit purée with a specific texture requires either the addition of thickening or gelling agents that act as texturing additives, or the application of elaborate heat or mechanical treatments such as draining and evaporation. The only purpose of these is to increase the viscosity of the pulp by concentration. However, these treatments cause a loss of flavours and juice, and sometimes a change in the colour of the pulp.

35 The invention overcomes this by using an apple or pear purée preparation process that consists of placing crushed fruit in conditions that inhibit its polygalacturonase activity in order to obtain inhibited pulp and to place the inhibited pulp in contact with a pectinesterase at a temperature of 10-60°C for a period of 15 minutes to 12 hours.

40 The in situ demethylation of the pectins through the action of exogenous pectinesterases enables products to be obtained which can have a whole range of textures, from a thick pulp to completely jellified. The enzymatic reaction makes the pectins sensitive to the presence of calcium ions and, if they are present, a three-dimensional network is formed within the purée, which leads to a profound change in the texture.

45 The procedure according to the invention enables the possibilities for jellifying purées rich in highly methylated pectins in systems with fewer sugars to be extended, without the addition of any gelling or thickening agent. The procedure therefore offers a great economic and nutritional benefit, as it enables the use of purées thus modified to be diversified in light foodstuffs, because it enables new products to be obtained with different textures and because it enables the juice to be salvaged.

5 The procedure of the invention does not require the addition of exogenous pectins, nor even of any thickening or gelling agent, in order to obtain new textures. It uses purified pectinesterases that do not appear in the fruit purée produced. This exogenous enzymatic action is different from the natural action of the products, as the polygalacturonase and possibly endogenous pectinesterase activity even need to be inhibited, for example by cooking prior to the enzymatic treatment. This inhibition of the natural enzymes is necessary to avoid the degradation of the pectins in the fruit by endogenous polygalacturonases.

10 The products studied by WILEY and LEE (1970) are fruit pieces, in other words a certain level of tissue integrity has to be maintained so that the calcium and possibly the pectinesterase can act. However, in this invention the integrity of the fruits is unnecessary and a fruit purée is preferred to ensure that the pectinesterase and calcium are well distributed. If the apple slices treated as described by WILEY and LEE are crushed, the textures produced by this invention are not obtained. Using a calcium (and pectinesterase) bath is not possible with an apple purée. Moreover, adding calcium by itself to the apple pulp does not result in as large an increase in viscosity as in the procedure of this invention. The two procedures are fundamentally different in terms of the action mechanism of the pectinmethyl esterase and the calcium. For apple pieces, WILEY and LEE showed that pectinmethyl esterase action only had a small effect on cell tissue in relation to that of calcium. In the invention, the enzyme has the main role, with calcium only playing a supplementary role in the development of the pulp's viscosity. Finally, the operating conditions (pH field, implementation of the procedure) are entirely different and require different technologies.

15 20 25 The invention also concerns an apple or pear purée, almost completely free from texturing additives, that has a pectin demethylation rate of less than 70%, a calcium content by weight greater than 300 parts per million and a Bostwick consistency index at 25°C of less than 2. This index demonstrates the thickened texture of the product.

30 The product obtained by the procedure of the invention is therefore characterised by:

- a thick texture obtained thanks to the action of a processing aid, pectinesterase, and without the action of any thickening or gelling agent such as alginates, guar gum, tragacanth, gum arabic, carrageenans, agar-agar, microcrystalline celluloses, and their derivatives, and more particularly pectins, with any degree of methylation. The product is not, however, incompatible with other food additives such as colourings, preservatives, antioxidants or flavourings, provided that in the doses used they do not interfere with the development of the viscosity of the product and that, if they are added at the beginning of the enzymatic reaction, they do not inhibit the activity of the pectinesterase,
- an average degree of methylation of the pectins present in the apple and pear purée of less than 70%, this parameter being determined by the method of SCHULTZ, T.H. (1965),
- a calcium concentration, determined by atomic absorption spectrometry, greater than 300 ppm,
- an improvement in the texture in relation to the initial product. The Bostwick index may reach any of the values lower than the initial values (down to an index of 0 unit), depending on reaction times, the calcium concentration and the acidity of the product. It is notably lower than 2.

35 40 45 50 For the enzymatic reaction by pectinesterase to be perfectly controlled, the enzymatic activity intrinsic to the pear and the apple must be inhibited, in particular polygalacturonase activity. This is achieved according to the invention by using procedures that are already known and, for example, by cooking crushed pears that have previously been washed. After crushing, the lumps may have an overall size of 1 cm by 2 cm. The cooking itself may be done in various ways, whether interrupted or continuous. For example, the crushed apples may be heated by direct low-pressure (0.3 bar)

steam injection, in a heating vat where the product is fed through by an auger conveyor. The temperature is increased to 95°C in 6 to 7 minutes. Until it leaves the heating vat, the product is cooled and it exits at around 90°C. Cooking can also be done by heating in a tubular heat exchanger at 92°C for 3-4 minutes. Extracting the juice (up to 10%) may be done by draining. The pomade is extracted by refining, i.e. by passing the product through a sieve. The refiner may, for example, be equipped with 2 sieves mounted in series, with mesh diameters (in mm) of 15/10 and (8/10 or 12/10) for apples, and 15/10 and 4/10 for pears. The pulp produced is then suitable to undergo enzymatic treatment after it is cooled to the desired temperature and after any addition of fruit juice or nectar. The product may be diluted with juice up to 50% of its weight.

10 The enzymatic hydrolysis of the pulp prepared as described is carried out with or without the presence of calcium salts (in any form but preferably in the form of calcium carbonate). Using calcium carbonate enables the pH to be adjusted to greater values and accelerates the enzymatic process. Calcium salts may be used at concentrations of 0.5-2 g/kg of pulp, with the acidity of the mixture and the calcium concentration determining the final level of jellification, which is measured by the Bostwick index. The acidity of the product is preferably lower than 7 g of malic acid equivalent per kg of pulp, as too much acidity hinders or even prevents the gelling of the pectins.

15 The refractive index of the product may also be adjusted to different values (up to 40°brix) by using sweeteners, juice concentrate during or after the enzymatic treatment, or any other ingredient that does not inhibit the enzymatic activity if it is added before the reaction.

20 The pH of the product may be between 3 and 4.5. It is chosen so that the enzyme can function and that, as far as possible, it will be close to the pH where the pectinesterase is most active. Although the pH may be adjusted again later, it is preferable to remain within the pH limits at which modified pectins can gel. For the apple pulp, care will be taken to remain at pH values slightly greater than 4. The acids freed during demethylation will therefore restore the pH to values that are entirely compatible with the hygienic quality of the product (pH < 4).

25 The temperature of the reaction is fixed by the optimum temperature for the action of the enzyme. It will be less than the inactivation temperature of the enzyme (< 70°C). Temperatures varying from 10 to 60°C may be applied, though the most beneficial are temperatures of 40-50°C.

30 All of the ingredients are carefully homogenised before the enzyme is added. The pectinesterase concentration determines the reaction speed; the reaction times can be between 15 minutes and 12 hours, and preferably from 1 to 3 hours. Any purified pectinesterase (i.e. free of polygalacturonase activity) may be used, but preferably the pectinesterase RAPIDASE CPE, sold by Gist-Brocades (France), at concentrations of 0.1-10 ml/kg of pulp, and preferably 0.3-1.0 ml/kg of pulp.

35 40 Depending on the desired texture and the packaging of the product, the pectinesterase action can be produced according to two distinct procedures:

1. Without stirring: after the pulp and the ingredients have been homogenised, the whole mixture is enzymated and decanted into packaging pots (small cup type). These are then conveyed to an incubation chamber at the desired temperature. When the texture is correct (i.e. when the gelling point is reached or the pulp is considered sufficiently thick), the enzymatic activity is inhibited by pasteurising the pots.

2. In a system with stirring: the action of the pectinesterase is produced in the mixing vat, while the mixture is being stirred. After hydrolysis, the product is conveyed to the pasteurisation system, and then packaged.

5 After the enzymatic reaction and pasteurisation, the product may be consumed as it is or incorporated into any food preparation, for example mixed with fruit purées that have too weak a consistency.

10 According to another use of the invention, the enzymatic demethylation is carried out without calcium salt and with or without sweetening. The calcium and any sweeteners can then be added either before or after pasteurisation. The calcium salts are, however, more effective in increasing the viscosity of the product when they are added before pasteurisation. This process has the benefit that it only increases the viscosity of the product after it is cooled in the packaging containers, and therefore limits the power required by the equipment to handle and circulate the product. However, 15 the calcium salts must be perfectly distributed within the product so that it is homogenous and a slight loss of effectiveness is noted in the system in these conditions.

The following examples illustrate the invention. The characteristics indicated in these examples are determined as follows:

20

- Brix:

The brix (or refractive dry matter content) is determined by refractometry at 25°C.

- Acidity:

25 The acidity of the pulps is determined by titration of a 5 g sample up to a pH of 8.2 by the addition of 0.05 N soda. The acidity expressed in g of malic acid equivalent per kg of pulp is obtained using the following equation:

$$\text{Acidity} = (\text{NaOH} \times 1000W/W_{\text{sample}})$$

W being the exact weight of the sample

30

$W_{\text{sample}}$  being the weight of the sample in the furnace

- Calcium content:

2 g of fresh matter are weighed in a preloaded platinum crucible. This ensemble is placed in the incubator at 60°C for one night, then 2 hours at 102°C followed by 6 hours in the furnace at 550°C.

35

The ashes are placed in 2 to 3 ml of HNO<sub>3</sub>, 0.5N. They are dissolved by heating under a watch glass, then the mixture is filtered and brought to 20 ml. The calcium is measured by atomic absorption spectrometry with LaCL<sub>3</sub> as a spectral buffer.

- Degree of esterification of the pectins:

40

The degree of esterification of the pectins (which corresponds to their methylation level) is determined by the method of SCHULTZ, T.H., described in "Methods in Carbohydrate Chemistry", R.L.WHISTLER ed., 1965, 5, 189, Acad. Press.

- Consistency of the pulp:

45

The texture of the pulp is assessed using the Bostwick consistometer at 25°C. The reservoir is carefully filled with pulp and the barrier is raised to point 0, in order to enable the product to flow. One minute later, the length of the flow is measured (using the Bostwick index). The test is carried out using the Bostwick consistometer that can be purchased from CSC Scientific Company Inc. The equipment comprises a tank divided into two sections by a barrier. One of the sections acts as a

reservoir. The base of the other is sloping, which enables the distance travelled by a product, in a given time after the barrier is raised, to be measured.

Example 1: Production of a sugared, jellied apple pulp in small cups.

Apples are crushed into lumps of 1 cm x 2 cm and then cooked by 0.3 bar steam injection. The temperature is raised to 95°C in six minutes. 10% of the juice is extracted by draining, then the pomade is separated by refining by passing first through a 15 mm mesh sieve then a 10 mm mesh sieve. 350 kg of apple juice at 12°brix are added to 3500 kg of drained pulp at 12°brix, and the mixture is cooled to 50°C. 605 kg of crystallised sugar and 3.5 kg of calcium carbonate are then added, followed by 1.75 l of rapidase CPE pectinesterase and 0.5 kg of ascorbic acid. The product thus produced is placed in small cups and incubated at 50°C for 4 hours, then it is pasteurised to produce a perfectly jellified apple purée (Bostwick index = 0) with a brix of 24.5 and an acidity of 3 g of malic acid equivalent/kg of pulp. The final pH is 3.8. The calcium concentration is 292 mg/kg of fresh matter, i.e. 1192 mg/kg of dry matter, and the degree of esterification of the pectins is 26%.

Example 2: production of a thick sugared apple purée

The procedure takes place as in example 1, except that the product is not packaged in small cups after enzyming. Packaging takes place after pasteurisation. While the inhibited pulp is placed in contact with the pectinesterase, it is stirred at 100 tr/mn.

The results obtained are shown in table I.

25

Table I

Time (in hours)	Brix	pH	Acidity (g acid/kg)	Bostwick
0	25.1	4.01	2.66	6.25
1	25.1	3.92	2.84	6.2
2	25.3	3.87	3.03	4.75
3	25.1	3.84	3.00	2.5
4	25.3	3.81	2.66	0.25

After four hours of the enzymatic reaction, the pulp produced is perfectly jellified. It can be used as it is or mixed with pulps with a weaker consistency (see example 3). Its  $\text{Ca}^{2+}$  content is 1241 mg/kg of dry matter and the degree of esterification is 32%.

Example 3: Production of a varied range of textures by mixing pulp textured according to the process with pulp with an overly weak consistency as indicated in table II.

35

Table II

Proportion of normal pulp in the jellified pulp	Final Bostwick level	Ca concentration (ppm)	Degree of methylation (in %)
0%	0.00	1280	32
10%	0.25	1053	39
30%	1.00	828	49

50%	2.75	705	61
100%	4.75	217	89

Incorporating jellified pulp into pulps with a weaker consistency enables the texture of the latter to be improved. The taste and colour of the product are not altered.

## CLAIMS

1. Procedure for the preparation of an apple or pear purée, characterised by the fact that it consists of placing crushed fruit in conditions that inhibit its polygalacturonase activity in order to produce inhibited pulp and to place the inhibited pulp in contact with a pectinesterase at a temperature of 10-60°C for a period of 15 minutes to 12 hours.  
5
2. Procedure according to claim 1, characterised by the fact that it consists of placing the inhibited pulp in contact with a pectinesterase at a pH of 3-4.5  
10
3. Procedure according to claim 1 or 2, characterised by the fact that it consists of adding 0.5-2 g of calcium salt per kg of pulp to the inhibited pulp, before or after it is placed in contact with a pectinesterase.  
15
4. Procedure according to one of claims 1 to 3, characterised by the fact that it consists of adding 0-50% by weight of fruit juice or nectar to the inhibited pulp.  
20
5. Procedure according to one of claims 2 to 4, characterised by the fact that it consists of inhibiting the polygalacturonase activity by heating the crushed fruit to a temperature of at least 80°C for at least two minutes.  
25
6. Procedure according to claim 5, characterised by the fact that it consists of inhibiting polygalacturonase activity by heating the crushed fruit to a temperature of 90-95°C for 3-4 minutes.  
7. Apple or pear purée, almost completely free from texturing additives, characterised by a pectin methylation level of less than 70%, by a calcium content by weight greater than 300 parts per million and by a Bostwick consistency index at 25°C of less than 2.

REPUBLIC OF FRANCE

NATIONAL INSTITUTE OF  
INDUSTRIAL PROPERTY

## RESEARCH REPORT

drawn up on the basis of the latest  
claims filed before the beginning of  
the research

National registration number

FR 9300294  
FA 481026

DOCUMENTS CONSIDERED RELEVANT		Claims related to the application examined
Category	Document reference with an indication of the relevant parts, if necessary	
A	FLUESS. OBST vol. 41, no. 7, 1974, pages 282-284 G. VOORDOUW ET AL * page 283, table 1, preparation D *	1
A	US-A-5 007 334 (G.W. KOBES ET AL) * column 2, line 35 – line 44 *	1
A	BE-A-642 994 (A.F. MURCH ET AL) * page 22, line 17 – line 28 *	1
T	WO-A-9 309 683 (GIST-BROCADES NV) -----	
TECHNICAL FIELDS RESEARCHED (Int. CLS)		
A23L		
Date of completion of the research 30 AUGUST 1993		Examiner VAN AMSTERDAM L.
CATEGORY OF DOCUMENTS CITED		T: theory or principle on which the invention is based E: patent document dated later than the date of filing and which was only published on the date of filing or a later date D: cited in the application L: cited for other reasons ..... &: member of the same family, corresponding document
X: particularly relevant in itself Y: particularly relevant combined with another document of the same category A: relevant to at least one claim or to the general technological background O: non-written disclosure P: supplementary document		